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(54) Title: ABSORBENT FOOTWEAR MATERIAL

(57) Abstract

An open cell polyurethane, non-swelling foam impregnated or coated into a non-woven fabric, comprising super absorbent ingredient particles. The disclosed material is a super absorbent, fluid locking, moldable footwear product that takes body fluids away from the surface, and gels or locks the fluids in place even while under pressure. The material is breathable and releases fluids through evaporation.

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ABSORBENT FOOTWEAR MATERIAL

Field of the Invention

This invention relates to a liquid locking, moldable, non-swelling, polyurethane foam impregnated into a non-woven fabric. More particularly, it relates to a durable, liquid absorbent, non-swelling, compression moldable composite material that locks in fluids when subjected to pressure.

Background of the Invention

The problem of moisture collecting in shoes, boots, and other footwear has long been a problem in the footwear art. Moisture released by the foot, if not wicked away, can cause discomfort, temperature variances, blisters, and fungus growth.

Typically, the moisture problem has been addressed by incorporating a moisture-wicking liner in the footwear product. Such liners are often made from textile and nonwoven materials or a combination of both.

Foam footwear insoles are well-known in the art, typically being comprised of a laminate comprising a liner material as a top layer, a foam or other cushioning material, and a stiffener underneath the foam and liner layers. The foams are typically polyurethane or polyethylene foams. Current footwear insoles foams are resilient and provide a shock-

components of the insoles of the prior art do not provide for wicking of moisture away from the foot and subsequent locking of the moisture in the insole.

The use of foams made from hydrophilic polymers as cushioning and absorptive insoles for footwear is one possible solution to the above problem. However, footwear insoles comprised of foams made from hydrophilic polymers have significant disadvantages. Swelling occurs upon liquid absorption in almost all polymeric foam compositions made from hydrophilic polymers. In these foams, i.e., those which use a hydrophilic polymer, absorption takes place in the polymer, which therefore swells. The swelling disfigures the thickness of the product, which is a problem in the limited volume of a shoe cavity. Further, changes in dimensions of the foam can cause stress on the junction of the foam with the other elements of the footwear material, increasing wear. Also, it would be beneficial to have a material which absorbs liquid only upon the application of pressure, thus limiting absorption of moisture from, for example, a humid environment when the footwear product is not being worn. Thus, there is a need for a liquid retaining, compression moldable composite foam material that does not swell and which absorbs moisture only upon application of pressure for use as a footwear insole and/or as a shoe and boot liner.

Until the present invention, there was no known polyurethane material that, when contacted with moisture, wicks it from the surface and locks it in place upon application of pressure to the material. The non-swelling absorbent capacity of the present invention is another surprising and unexpected result of the novel composition of the present invention, providing results superior to the absorbent materials of the prior art.

The novel composition of the polyurethane foam of the present invention is also surprising and unexpected. Methylenediphenyl diisocyanate is a non-hydrophilic prepolymer which, when incorporated into a foam, would be expected to block off access of moisture to any incorporated superabsorbent polymers, and would thus be expected to create a foam which would not have liquid-locking capabilities. An absorbent foam based on methylenediphenyl diisocyanate which incorporates superabsorbent polymers was not known in the art prior to the present invention, and thus its unique properties were also not appreciated by the art.

Objects of the Invention

It is one object of the present invention to provide a hydrophilic polyurethane foam that is based on the non-hydrophilic prepolymer methylenediphenyl diisocyanate which comprises a superabsorbent polymer, and which absorbs fluid upon application of pressure.

It is a further object of the present invention to provide an absorbent cushioning footwear product comprised of a non-hydrophilic polyurethane foam which, when used as in insole or liner in a foot covering, serves to absorb moisture produced by the feet and thereby keep moisture away from the feet of the wearer of the foot covering.

Another object of the invention is to provide an absorbent, breathable cushioning footwear product which does not absorb moisture unless pressure is applied to the surface of the absorbent footwear product, and which continuously releases absorbed moisture by evaporation (i.e whether or not pressure is applied).

Summary of the Invention

The present invention is a durable, breathable, liquid absorbent, liquid locking, moldable composite material comprising a substrate and a polyurethane foam impregnated into or coated on the substrate, the polyurethane foam being made from a polyol, a non-hydrophilic prepolymer, a superabsorbent polymer and one or more surfactants.

The composite material can further comprise an acrylic polymer to impart moldability and compressibility characteristics to the material.

Detailed Description of the Invention

All patents and publications cited herein are hereby incorporated by reference. In the event of a conflict in terminology, the present disclosure is controlling.

The composite material of this invention is comprised of an open cell, polyurethane foam impregnated into or coated onto a woven or non-woven substrate. The polyurethane foam is the reaction product of a methylenediphenyl diisocyanate prepolymer and a polyol, surfactants, and optionally an acrylic polymer. The acrylic polymer, when added, is added in an amount sufficient to impart moldable characteristics to the foam. The

composite material further comprises one or more superabsorbent polymers that have either been mechanically attached to the non-woven fabric r incorporated into the polyurethane foam. In a preferred embodiment, the superabsorbent polymer is incorporated into the polyurethane foam. The composite material can also optionally comprise a needlepunched fiber finish which serves to disperse liquid to the interior of the foam and to impart surface structure to the composite material.

The superabsorbent polymer-containing polyurethane foam of the invention is prepared by mixing together one (1) part of a methylenediphenyl diisocyanate prepolymer and two (2) to six (6) parts of a polyol component. The polyol component contains a polyether polyol, surfactants, such as a propylene oxide/ethylene oxide block copolymer such as Pluronic L-62 (about 2-15% of polyol component by weight, preferably about 10% by weight), a 10% aqueous solution of a propylene oxide/ethylene oxide block copolymer such as Pluronic F-88 (about 0.25-3% of polyol component by weight, preferably about 2% by weight), one or more superabsorbent polymers (0.25-2% of polyol component by weight, preferably about 2% by weight) and, optionally, an acrylic polymer (.25-10% of polyol component by weight, preferably about 3% by weight). The acrylic polymer, when added, provides moldability to the finished product.

The prepolymer and polyol components are combined in the appropriate quantities and thoroughly mixed. A preferred method of mixing utilizes a foam machine of the type well-known in the art, with a mixing head rotating at between 2500 and 4000 rpm. The mixture is discharged into a substrate, preferably a carded, airlaid non-woven material, which has been positioned on top of a flat release material, such as silicone coated release paper (e.g. 92# Stay Flat L-3 Liner, Technicote/Siltech, Inc., Miamisburg, OH). The foam is sandwiched on top by another piece of the release material. The non-woven substrate can be a material such as 2.5 ounce/square foot Better Blend (Carlee Corporation, Rockleigh, NJ). The papers carrying the substrate travel horizontally at a speed determined to be sufficient to deposit an amount of the isocyanate/polyol mixture which will yield a product of the desired thickness.

The polymer is allowed to react with the polyol, yielding carbon dioxide and a polyurethane, causing a foam impregnated non-woven to form. The evolving gas is trapped

in the reacting mixture and form the cells of the foam. As more carbon dioxide gas is generated, the cells enlarge and the reactant mass expands proportionately, causing the foam to rise. At some point, the limiting reactant (isocyanate functional prepolymer) is depleted and gas generation halts, typically in 4 to 6 minutes. After about six minutes, the top and bottom release papers are continuously removed, exposing the composite material. The composite material is then moved into a forced air convection oven maintained at 220°F to 275°F in order to finish cure the material. Additional reactions occur such as chain extension and crosslinking to yield a "cured" three dimensional network of a non-hydrophilic polymer foam. When cured, the product is typically, but not limited to, from one-eighth inch to one-half inch in thickness. After curing, the material can be die cut to the desired shape and molded. The resulting material typically is capable of absorbing from about five to about twenty times its weight in water.

The chemical reactions occurring during polyurethane foam manufacture and continuous and discontinuous methods for such manufacture are discussed more fully in "Polyurethane Handbook, 2nd Edition" edited by Günter Oertel, Hanser Publishers, Munich, (pp. 11-244) 1993, herein incorporated by reference.

A preferred isocyanate prepolymer is Flexible Products isocyanate FP 100-A polyurethane prepolymer derived from methylenediphenyl diisocyanate. A preferred polyol for use in the polyol component is FP 100-B. Also preferred is FP 365-6 (Flexible Products, Marietta, GA). Preferred surfactants are Pluronic L-62 and Pluronic F-88 (BASF Corp., Charlotte, NC). A preferred acrylic polymer for use in the invention is Rhoplex TR407 emulsion (Rohm & Haas Co, Philadelphia, PA). Preferred superabsorbent polymers are characterized by being able to absorb from about 1000 to about 5000 percent by weight of aqueous solutions and to hold such fluid under pressures of up to about 80 psi without dewatering. Such superabsorbent polymers include crosslinked polyacrylate polymer, starch grafted polyacrylate polymer, crosslinked potassium polyacrylate/polyacrylamide, sodium salt of crosslinked polyacrylic acid polyalcohol graft copolymer, partial sodium salt of crosslinked polyacrylic acid, crosslinked polyvinyl pyrrolidone, crosslinked sulfonated polystyrene, crosslinked polysulfoethyl(meth)acrylate, crosslinked poly(2-ethylhexylacrylate), and crosslinked hydrolyzed polyacrylonitrile. A preferred superabsorbent polymer for use in the

material of the invention is AP80HS superabsorbent polymer (Stockhausen, Inc., Greensboro, NC).

In an embodiment in which the superabsorbent polymer is incorporated into the material of the invention by mechanical attachment, the polymer is generally attached to the non-woven using a pressure-sensitive cement or contact adhesive. The adhesive may be water born, solvent born, or hot melt. The amount of adhesive applied will be dependent on the amount of superabsorbent polymer which is to be attached, and can be readily ascertained by those of ordinary skill in the art. A non-limiting example of such an adhesive is Super 77 spray adhesive (3M Corporation, St. Paul, MN). The foam to be used in this embodiment does not contain superabsorbent polymers. This foam is prepared by the same method as the foam containing superabsorbent polymers, except that water is substituted for the superabsorbent polymer in the polyol component.

The composite materials of this invention can be further modified utilizing a needlepunching process that embeds and punctures fibers of a finish material into the foam material. This needlepunching process can enhance the performance characteristics of the product and provide the product with a finished surface, which can be beneficial for aesthetic as well as functional reasons. When present, a fiber finish material can aid in passing fluids to be absorbed into the underlying foam matrix. The fibers of the finish can be either hydrophilic or hydrophobic, and serve to guide or draw fluids into the foam matrix leaving a soft, dry surface. Nonlimiting examples of fibers which can be used in this finish of the present invention are acrylic, polypropylene, or polyester fibers, or a blend of these.

Example

A polyurethane foam was prepared by mixing together one (1) part of an isocyanate FP 100-A prepolymer and four (4) parts of a polyol component. The polyol component comprised polyol FP 100-B, Pluronic L-62 (10% by weight), a 10% aqueous solution of Pluronic F-88 (2% by weight), Rhoplex TR 407 (3% by weight) and superabsorbent polymer AP80HS (2% by weight). The two components were brought together in a mixing head at about 4000 rpm. The mixture was allowed to discharge into a carded, airlaid non-woven on top of a silicone coated release paper and sandwiched on top

by another silicone coated release paper. The papers traveled horizontally at 4 feet per minute, yielding a thickness of one-quarter inch in the product.

During the next four to six minutes, the polymer reacted with the polyol causing a foam impregnated non-woven to form. After six minutes the top and bottom release papers were continuously removed from the top surface, exposing the material. The product was then carried by a moving belt into a forced air convection oven maintained at 220°F for the purpose of finish curing. The resulting material was an open cell foam, impregnated non-woven, white in color, one-quarter inch thick, that was wettable when pressure was applied to the surface in contact with moisture.

What is claimed:

1. A durable, breathable, liquid absorbent, liquid locking, moldable composite material comprising:

a substrate;

a polyurethane foam impregnated into or coated on said substrate, wherein said polyurethane foam comprises a polyol, a non-hydrophilic prepolymer, a superabsorbent polymer and one or more surfactants.

2. The material of claim 1 wherein said polyurethane foam is formed by reaction of a non-hydrophilic isocyanate polymer and a polyol in a ratio in the range form 1:1 to about 6:1.

3. The material of claim 3 wherein said foam is comprised of Flexible Products FP100-A isocyanate and a member selected from the group consisting of Flexible Products FP 100-B polyol and Flexible Products FP 365-6 polyol.

4. The material of claim 1 wherein said polyurethane foam further comprises an acrylic polymer in an amount sufficient to impart moldability to said material.

5. The material of claim 1 wherein said material is capable of absorbing from five to twenty times its weight in water.

6. The material of claim 5 where in said material is compression moldable using standard equipment.

7. The material of claim 1 wherein said material is fiber needlepunched using an acrylic, polyester or polypropylene fiber blend that is hydrophobic or hydrophilic.

8. The material of claim 1 wherein said superabsorbent polymer is impregnated in said non-woven carded material.

9. The material of claim 1 wherein said superabsorbent polymer is a component f said polyurethane foam.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/10216

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B05D 1/12
US CL :428/308.4, 317.9
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/308.4, 317.9

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,281,437 A (SINGH) 25 January 1994, see entire document.	1, 2 & 4-9

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search 18 JULY 1997	Date of mailing of the international search report 25 AUG 1997
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Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/10216

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 3
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

Trade names with product numbers do not identify polymers in a manner that can be compared with prior art or in a manner in which a search can be determined.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark n Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.